

# Products Identified at an Alternative Disinfection Pilot Plant

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Many drinking water utilities have recently changed or are seriously considering changing their disinfection practice from chlorine to some alternative treatment process. However, most of these utilities are changing their disinfectants without evaluating chemical impacts. Therefore, a research cooperative agreement was developed with Jefferson Parish, LA, to evaluate four parallel streams treated with four different disinfectants (chlorine, monochloramine, chlorine dioxide, and ozone.) These streams, along with a fifth parallel stream, which was not treated with a disinfectant (control), were passed through both sand and granular activated carbon (GAC).

Ozonation reduced the total organic carbon (TOC) and total organic halide (TOX) concentration by 0.3 mg/L and 10 µg/L, respectively. The average concentration of TOC for the other disinfectants was comparable to that associated with the nondisinfected stream (3.3 mg/L). The average instantaneous TOX concentration for chlorine dioxide, chloramine, and chlorine disinfection after 30 min contact time increased by 60, 92, and 238 µg/L, respectively, from a nondisinfected concentration of 25 µg/L.

The volatile organics most affected by disinfection (chlorination) were the trihalomethanes. No significant change in concentration was noted after disinfection for the other volatile organics evaluated, such as 1,2-dichloroethane, dichloromethane, trichloroethylene, 1,1,2-trichloroethane, and carbon tetrachloride. Ozonation produced an average concentration reduction of 11 to 84% for most of the nonvolatiles evaluated. Conversely, a concentration increase of 43 to 100% was noted, after chlorination, for some of the nonvolatile organics.

## Introduction

Many drinking water utilities have recently changed or are seriously considering changing their disinfection practice from chlorine to some alternative treatment process. This type of treatment decision is primarily a result of regulations to control trihalomethanes (1). However, most of these water utilities have changed to alternative disinfectants without evaluating possible chemical impacts.

Various river systems provide the water source for many of these drinking water utilities. One such river is the Mississippi. In its 2400 mile course to the Gulf of Mexico, this river drains nearly two-thirds of the continental United States. At the end of this river is Jefferson Parish, LA, where a research cooperative agreement was developed to evaluate four parallel streams treated with four different disinfectants (chlorine, monochloramine, chlorine dioxide, and ozone). These streams, along with a fifth parallel stream, which was not treated with a disinfectant (control), were evaluated for chemical constituents, microbiological changes, and health effects.

## Research Objectives

A portion of the research effort at Jefferson Parish, LA, was developed to investigate the chemical and health effects of disinfectants and disinfection by-products. The objectives of this 1-year study were to identify chemical and biological contaminants in filtered water before disinfection, to evaluate chemical by-product formation and biological effects after disinfection, to compare the effectiveness of granular activated carbon (GAC) to the effectiveness of sand filtration for removing chemical contaminants, to evaluate the effects of post-adsorption disinfection with monochloramine and free chlorine on the pilot column effluents, and to collect samples for evaluating the health effects of the four disinfectants used in the pilot plant study (2). This last activity is not reported in this paper.

## Pilot Plant

Raw river water from the Mississippi River was pumped to the full-scale (Permutit III) plant where it was clarified with diallyldimethylammonium chloride and/or dimethylamine-type cationic polymers (3). After fluoridation, but before any disinfection, a portion of the clarified water was filtered through pressure sand filters and split into five process streams (Fig. 1). Each disinfected process stream consisted of a contact chamber

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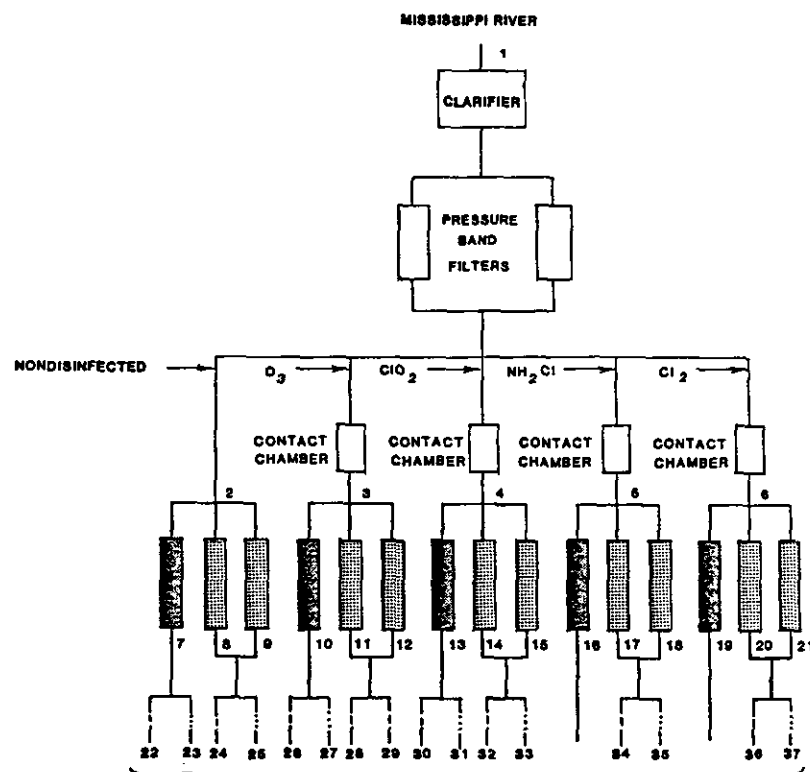


FIGURE 1. Flow schematic of Jefferson Parish, LA, pilot plant.

followed by parallel filtration through a sand column, a GAC column, and a duplicate GAC column. The non-disinfected process stream was identical to the disinfected process streams except for the elimination of the contact chamber.

Each disinfectant contact chamber had a 12.75-in. outside diameter (OD) and was constructed of stainless steel with stainless-steel flanged or capped ends. The chlorine, chloramine, and chlorine dioxide contact chambers were 10 ft high, producing approximately 30 min of disinfectant contact time with a flow of 2 gal/min (GPM). The ozone contact chamber was 11 ft high with countercurrent operation consisting of water entering at the top of the contact chamber and ozone gas entering at the bottom. The water and ozone gas influent lines were oriented so that the influent water would be in contact with the ozone gas stream for approximately 30 min. The other disinfectant contact chambers were operated in a cocurrent plug-flow mode.

Each pilot column had a 6-in. inside diameter (ID) and was 10 ft high. The pilot columns were charged with 6.8 ft of either sand or GAC to obtain a 20-min empty-bed contact time with a flow of 0.5 GPM. A portion of the process streams was collected in bottles and re-disinfected with chlorine or chloramine after passing through the pilot GAC columns.

## Disinfectant Residuals

The average disinfectant contact time for the 1-year operational period was 31.8, 31.4, 32.1, and 31.7 min,

Table 1. Average 30-min disinfectant residuals of each disinfectant stream.

| Process stream   | Disinfectant constituents    | Average residual, mg/L            |
|------------------|------------------------------|-----------------------------------|
| Ozone            | Ozone ( $O_3$ )              | 0.5 as $O_3$ (0.7 as $Cl_2$ )     |
| Chlorine dioxide | Chlorite ( $ClO_2^-$ )       | 0.6 as $ClO_2^-$ (1.3 as $Cl_2$ ) |
|                  | Chlorine dioxide ( $ClO_2$ ) | 0.5 as $ClO_2$ (1.3 as $Cl_2$ )   |
|                  | Monochloramine ( $NH_2Cl$ )  | 0.2 as $NH_2Cl$ (0.1 as $Cl_2$ )  |
|                  | Dichloramine ( $NHCl_2$ )    | 0.1 as $NHCl_2$ (0.1 as $Cl_2$ )  |
| Chloramine       | Chlorine ( $Cl_2$ )          | 0.1 as $Cl_2$                     |
|                  | Monochloramine               | 2.1 as $NH_2Cl$ (1.4 as $Cl_2$ )  |
|                  | Dichloramine                 | 0.4 as $NHCl_2$ (0.3 as $Cl_2$ )  |
| Chlorine         | Chlorine                     | 0.0 as $Cl_2$                     |
|                  | Chlorine                     | 1.0 as $Cl_2$                     |
|                  | Dichloramine                 | 0.3 as $NHCl_2$ (0.2 as $Cl_2$ )  |
|                  | Monochloramine               | 0.2 as $NH_2Cl$ (0.1 as $Cl_2$ )  |

respectively, for chlorine, monochloramine, chlorine dioxide, and ozone. From this contact time, an average residual of 1.0 mg/L chlorine, 2.1 mg/L monochloramine, 0.5 mg/L chlorine dioxide, and 0.5 mg/L ozone was maintained by daily testing 5 days per week (Table 1). These concentrations are comparable to the residuals produced by many water utilities. After addition of the

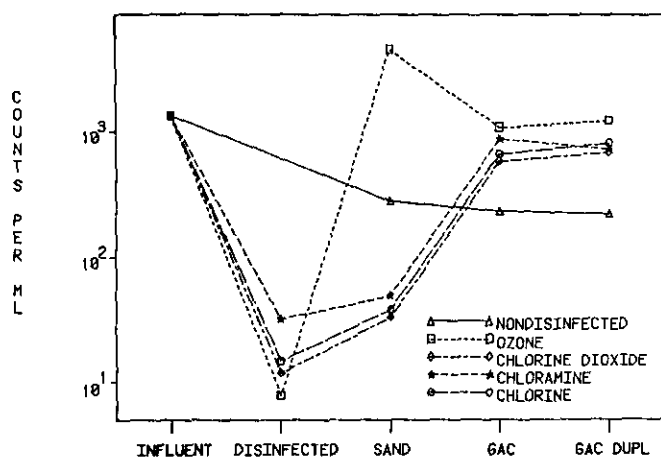


FIGURE 2. Average geometric means of heterotrophic bacteria, Jefferson Parish, LA, pilot plant.

various disinfectants, the pH changed no more than 0.1 units from the median influent pH of 7.5. The chlorine, chlorine dioxide, and monochloramine concentrations changed only slightly after sand filtration, but ozone was dissipated. No residual concentrations were detected for any of the systems after GAC filtration.

All the disinfectants except ozone had other associated disinfection products (Table 1). Chlorine, for instance, had an average monochloramine residual of 0.2 mg/L and an average dichloramine residual of 0.3 mg/L attributable to the presence of 0.1 to 0.2 mg/L of ammonia nitrogen. Also, chlorite was present in the chlorine dioxide residual at a concentration of 0.6 mg/L as compared to 0.5 mg/L for the chlorine dioxide. Essentially all the chlorite resulted from reduction of chlorine dioxide.

Ozone was generated from compressed dry air using an electrically powered ozone generator with a maximum output capacity of 0.25 lb/day. Chlorine dioxide was generated using sodium chlorite and sodium hypochlorite with sulfuric acid added to adjust the pH to 4. A 96% yield of chlorine dioxide was obtained. Chlorine gas was fed to both the chloramine and chlorine process streams. Ammonia was added to the chloramine process stream in the form of an ammonium hydroxide solution prior to the chlorine eductor.

## Disinfectant Effectiveness

After approximately 30 min disinfectant contact time, ozone had the highest level of disinfection relative to standard plate count (SPC), followed by chlorine dioxide, chlorine, and chloramine. After sand filtration, chlorine dioxide, chlorine, and chloramine produced similar counts of about 50/mL. The geometric mean for the SPC increased from 8 counts/mL to 4594 counts/mL for the effluent of the ozonated sand column, indicating biological activity on the sand column (Fig. 2). The geometric mean of the SPC in the GAC effluent of each disinfectant system increased dramatically to a level

Table 2. Number of positive coliforms, Jefferson Parish, LA, pilot plant.<sup>a</sup>

|                        | Positive coliforms |       |                  |            |          |
|------------------------|--------------------|-------|------------------|------------|----------|
|                        | Nondisinfected     | Ozone | Chlorine dioxide | Chloramine | Chlorine |
| 30-min contact         | 149 <sup>b</sup>   | 0     | 2                | 1          | 1        |
| Sand effluent          | 91                 | 1     | 2                | 0          | 1        |
| GAC effluent           | 125                | 3     | 3                | 7          | 8        |
| GAC duplicate effluent | 127                | 0     | 5                | 4          | 11       |

<sup>a</sup> 159 samples (3 samples per week for 53 weeks).

<sup>b</sup> No contact chamber and no disinfection.

(10<sup>3</sup> counts/mL), similar to the nondisinfected influent water of the pilot column systems.

Some positive total coliform were observed (Table 2). Those detected in the disinfection systems influent and sand filter effluent are suspected of being sample error. Most of the positive samples observed in the GAC columns occurred at the start of the pilot plant.

## Organic Surrogate By-Products

Two organic surrogates, TOC and TOX, were evaluated for the disinfectant systems. The TOC concentrations for each disinfectant stream after 30 min contact time were similar. Average values for these streams were 3.3, 3.0, 3.3, 3.4, and 3.3 mg/L, respectively, for the nondisinfected and the ozone, chlorine dioxide, chloramine, and chlorine disinfected streams. Although these concentrations have not been evaluated statistically, ozone appears to effect a slight TOC reduction (3.3 mg/L vs. 3.0 mg/L), possibly in part because of aeration.

When these disinfectant streams were passed through sand columns, only the ozone stream showed a TOC concentration reduction. The average TOC concentration in the effluent sand column was 2.5 mg/L, whereas the concentrations for all other disinfected stream effluents were comparable to their influent values. The average reduction of TOC across the ozone stream sand column was 0.5 mg/L, attributable to biological activity on the sand. This same phenomenon was observed in GAC columns. At approximately 180 days, steady-state conditions occurred, whereby all disinfected streams had a GAC effluent concentration of about 2.7 mg/L except for ozone, for which the GAC effluent concentration was approximately 2.2 mg/L.

The instantaneous TOX concentration for the nondisinfected stream averaged 25 µg/L. This same water ozonated with 30 min contact time produced an average concentration of 15 µg/L, indicating that some oxidation occurred. Subsequent tests showed that aeration also contributed to this reduction. The average instantaneous TOX concentration for chlorine dioxide, chloramine, and chlorine after 30 min contact time was 85, 117, and 263 µg/L, respectively. Figure 3 illustrates the relative differences in TOX concentration after disinfection during the 1-year test period. When results from the nondisinfected stream were subtracted from results

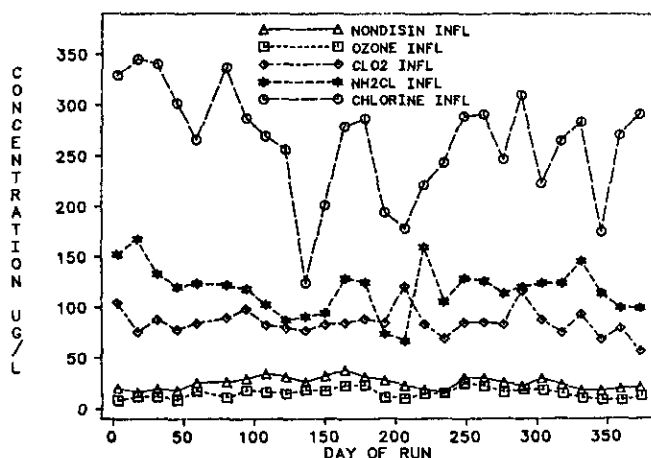


FIGURE 3. TOX concentrations after 30 min contact time, Jefferson Parish, LA, research project.

from the disinfected streams, an average instantaneous TOX by-product formation of 60, 92, and 238  $\mu\text{g/L}$ , respectively, was calculated. Conversely, ozone disinfection did not produce any instantaneous by-products but actually reduced the concentration by 10  $\mu\text{g/L}$ , possibly in part because of aeration.

The concentration of instantaneous TOX in the sand column effluent of each disinfection system was comparable to their respective influents. Average TOX concentrations were 23, 14, 83, 117, and 258  $\mu\text{g/L}$ , respectively, for the nondisinfected and the ozone, chlorine dioxide, chloramine, and chlorine disinfected effluents. The concentration of instantaneous TOX in the GAC effluents was influenced by the amount applied to the columns. The higher the influent concentrations (Fig. 3), the faster the breakthrough, and the higher the effluent TOX concentrations.

Most treatment plants that use ozone or chlorine dioxide use these disinfectants as pre-disinfectants and normally add them to raw water. To maintain a disinfectant residual in the distribution system, either chlorine or monochloramine is usually added after treatment. Samples from the pilot plant were stored for 5 days to simulate the end of a distribution system. These samples from each system were maintained with a chlorine and/or monochloramine residual; however, the residuals were higher than those which would be expected in a water treatment system.

The 5-day terminal TOX concentrations produced from the chlorine residual samples were significantly higher than the instantaneous values. Figure 4 shows the average TOX concentrations for three levels of treatment. Ozone and chlorine dioxide pretreatment reduced the available TOX precursor. The total 5-day concentration of TOX was reduced using GAC compared to conventional sand filtration for all disinfection systems. Those samples stored with a monochloramine residual showed a slight increase in TOX concentration for some systems and a decrease in other systems.

## Organic Profile

Flame ionization detection and electron capture chromatograms were used to provide an overall indication of the effect of using various disinfectants. As shown in Figure 5, chlorination appears to produce the most peaks in the low to medium molecular weight range followed by chloramination, chlorine dioxide, and ozone, compared to nondisinfected water. In the higher molecular weight range, two peaks that are present in the other chromatograms do not appear after ozonation. These general observations are discussed in the following sections. Data presented in this discussion were produced by using EPA-approved analytical procedures documented in an approved quality assurance plan (4).

## Volatile Organics

### Trihalomethanes

The trihalomethane (THM) species formed during the various disinfection processes were chloroform > bromodichloromethane > dibromochloromethane > bromoform. Chloroform accounted for about 75% of the THMs, with very little dibromochloromethane and relatively no bromoform formed. After 30 min contact time, average THM concentrations were 1  $\mu\text{g/L}$  for the ozone system, 1  $\mu\text{g/L}$  for the chlorine dioxide system, 4  $\mu\text{g/L}$  for the chloramine system, and 34  $\mu\text{g/L}$  for the chlorine system. The nondisinfected system had 1  $\mu\text{g/L}$  of THM. The THM formed by chlorination was removed by GAC for about 60 days until breakthrough; for chloramine, the removal was about 80 days until breakthrough.

Five-day average THM concentrations for sand filtration and GAC effluent streams that have been chlorinated are shown in Figure 6. Only after GAC has removed THM precursors is the concentration close to the promulgated standard of 0.10 mg/L. Subsequent disinfection of these same effluents with chloramine instead of chlorine produced lower average THM concentrations.

### Other Volatile Organics

The concentrations of 1,2-dichloroethane (DCE) in the nondisinfected influent to the column system ranged from below detection limit (0.1  $\mu\text{g/L}$ ) to 7  $\mu\text{g/L}$ . A disinfectant contact time of 30 minutes with ozone, chlorine dioxide, chloramine, and chlorine produced no significant change in DCE concentration. This was also the case for the sand column effluents of each disinfectant process stream. Effluent concentrations of the nondisinfected, ozone, chlorine dioxide, and chloramine GAC column were similar. DCE concentrations for the chlorine GAC column was higher after breakthrough, possibly because of desorption.

Other volatile organics detected in the influent were dichloromethane, trichloroethylene, 1,1,2-trichloroethane, and carbon tetrachloride. These compounds occurred infrequently at concentrations below 0.1  $\mu\text{g/L}$ .

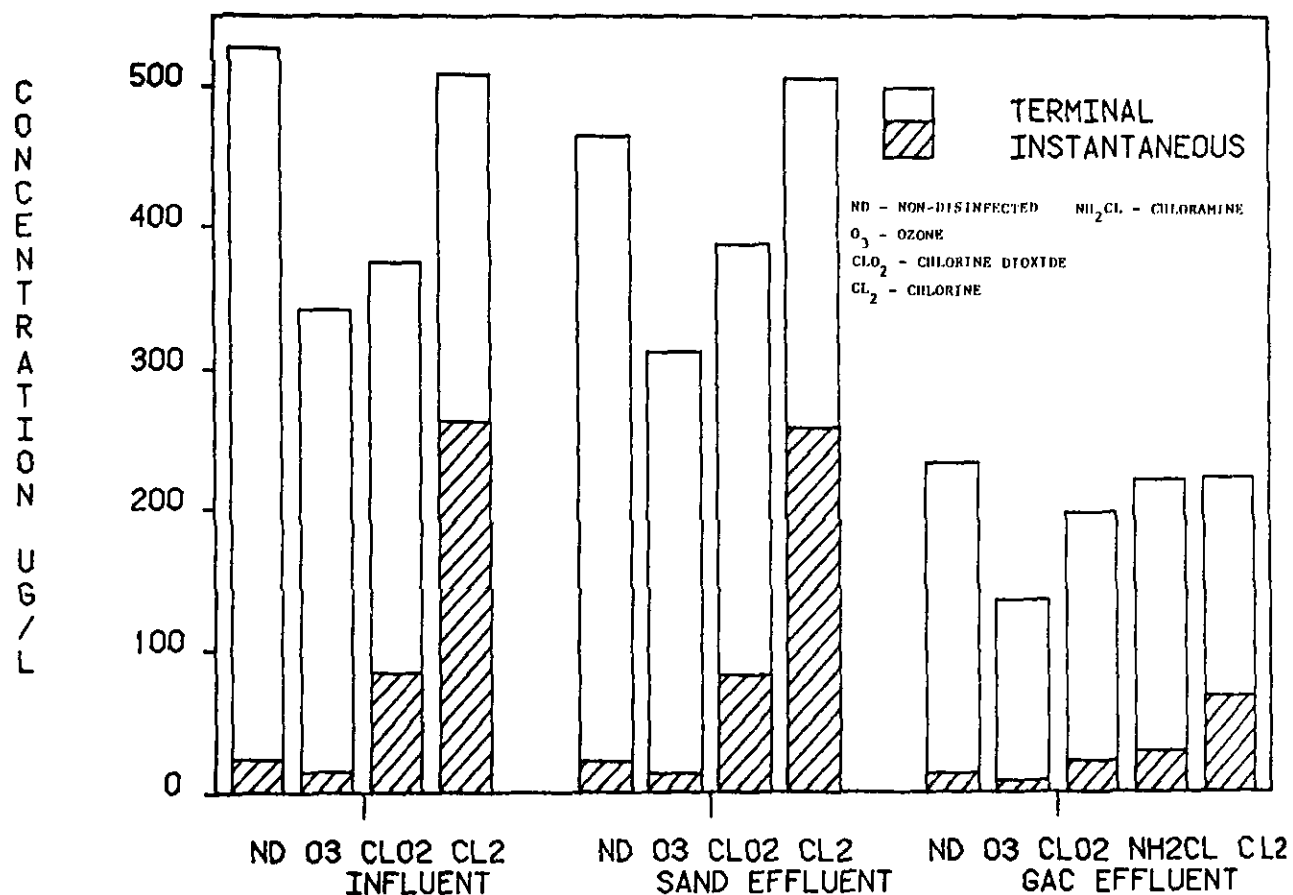


FIGURE 4. Average 5-day terminal TOX (Cl<sub>2</sub> at 28°C), Jefferson Parish, LA, pilot plant.

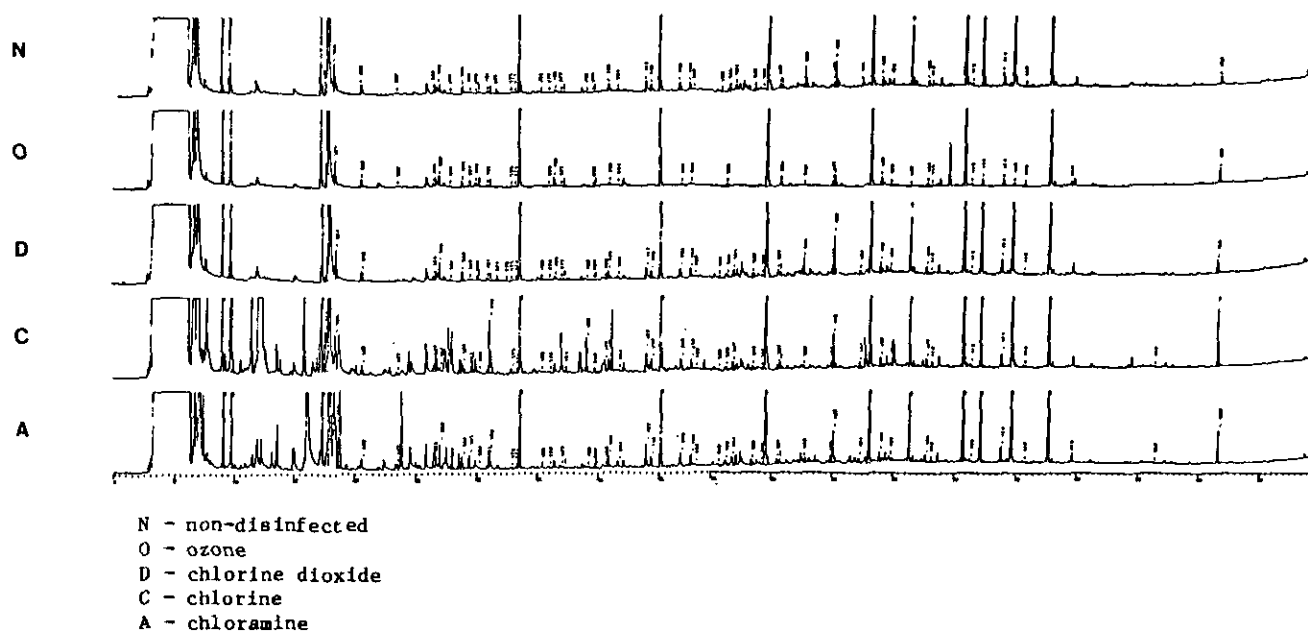


FIGURE 5. FID chromatograms, Jefferson Parish, LA, research project.

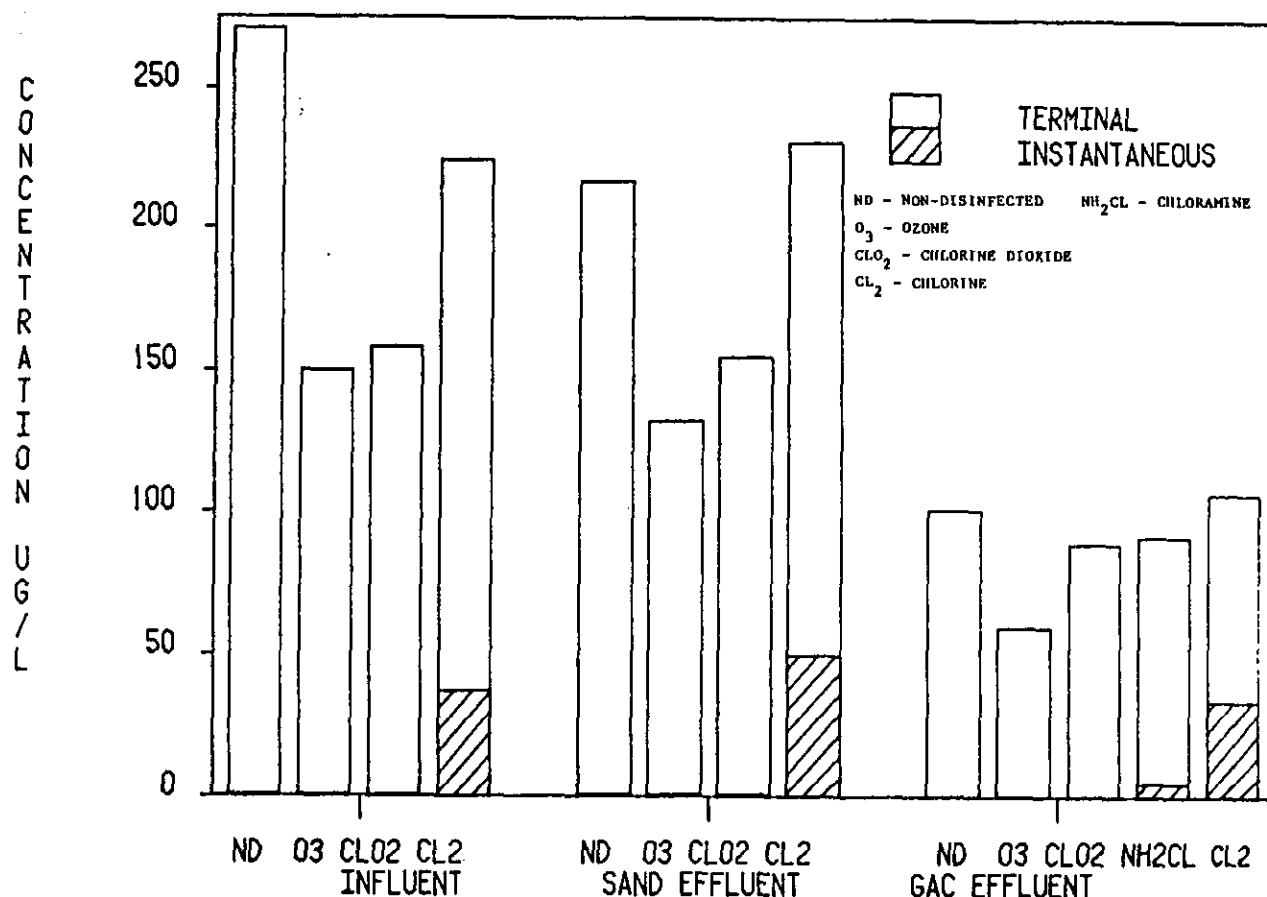


FIGURE 6. Average 5-day terminal THM ( $\text{Cl}_2$  at  $28^\circ\text{C}$ ), Jefferson Parish, LA, pilot plant.

except for one occurrence of trichloroethylene at  $20 \mu\text{g/L}$ . The concentration of these organics did not appear to increase after disinfection.

## Nonvolatile Organics

### Chlorinated Hydrocarbons

The herbicide atrazine and the insecticide alachlor were present in the influent to the pilot system throughout the study. Influent atrazine concentrations ranged from 23 to  $249 \text{ ng/L}$ , with an average of  $80 \text{ ng/L}$ . The influent atrazine concentration was not affected by chlorine dioxide, chloramine, or chlorine disinfection. However, ozonation produced an average atrazine removal of 83% relative to the nondisinfected influent. No change in concentration was noted after sand filtration. GAC filtration removed the atrazine (95-97%) throughout the 1-year operational period.

Alachlor levels in the nondisinfected influent of the pilot column system ranged from 13 to  $593 \text{ ng/L}$  with an average of  $127 \text{ ng/L}$ . As with atrazine, alachlor was also unaffected by chlorine dioxide, chloramine, or chlorine disinfection, but its concentration was reduced an average of 84% by ozonation. The sand column ef-

fluent was comparable to its influent. GAC removed 94 to 97% of the alachlor with no evidence of breakthrough during the study.

Other chlorinated hydrocarbon insecticides (CHI) were evaluated as a total sum of all the individual CHIs monitored during the study except atrazine and alachlor. Table 3 lists the CHIs with their frequency of occurrence and the minimum, maximum, and average concentrations at which they were detected. The total CHI concentration in the nondisinfected influent to the pilot column system ranged from 18 to  $88 \text{ ng/L}$  with an annual average of  $36 \text{ ng/L}$ . The concentration of these substances was unchanged after disinfection except in the case of ozonation, which produced an average total CHI reduction of 57%. Sand filtration had no effect on the CHI concentration. GAC removed the CHI from 90 to 93% over the 1-year operational period.

### Total Alkylbenzene

The specific alkylbenzenes grouped to form the total alkylbenzenes evaluated during the study are shown in Table 4. The total alkylbenzene concentration in the nondisinfected influent ranged from 59 to  $10,300 \text{ ng/L}$  with an average of  $590 \text{ ng/L}$ . A 30-min disinfectant con-

**Table 3. Concentration of chlorinated hydrocarbon insecticides in the nondisinfected influent.**

| CHI                       | Frequency, % | Concentration, ng/L |      |      |
|---------------------------|--------------|---------------------|------|------|
|                           |              | Min                 | Max  | Avg  |
| Aldrin                    | 100          | 0.20                | 0.92 | 0.53 |
| $\alpha$ -BHC             | 100          | 1.14                | 6.75 | 2.78 |
| $\beta$ -BHC              | 100          | 0.87                | 3.33 | 1.64 |
| $\gamma$ -BHC             | 100          | 0.40                | 9.06 | 1.39 |
| $\alpha$ -Chlordane       | 100          | 0.12                | 0.47 | 0.27 |
| $\gamma$ -Chlordane       | 100          | 0.15                | 0.55 | 0.31 |
| Oxychlordane              | 92           | 0.02                | 0.35 | 0.09 |
| $\alpha$ -Chlordene       | 89           | 0.02                | 0.46 | 0.14 |
| $\beta$ -Chlordene        | 93           | 0.08                | 32.5 | 7.55 |
| $\gamma$ -Chlordene       | 96           | 0.06                | 0.77 | 0.43 |
| DCPA <sup>a</sup>         | 100          | 0.17                | 5.42 | 1.42 |
| <i>o</i> , <i>p</i> '-DDD | 100          | 0.13                | 1.13 | 0.44 |
| <i>m</i> , <i>p</i> '-DDD | 56           | 0.03                | 1.34 | 0.36 |
| <i>p</i> , <i>p</i> '-DDD | 93           | 0.17                | 1.28 | 0.57 |
| <i>o</i> , <i>p</i> '-DDE | 96           | 0.08                | 0.83 | 0.30 |
| <i>p</i> , <i>p</i> '-DDE | 100          | 0.06                | 0.32 | 0.16 |
| <i>o</i> , <i>p</i> '-DDT | 59           | 0.03                | 7.80 | 0.68 |
| <i>p</i> , <i>p</i> '-DDT | 85           | 0.07                | 1.25 | 0.36 |
| Dieldrin                  | 100          | 1.63                | 5.80 | 2.84 |
| Endosulfan-2              | 96           | 0.02                | 0.72 | 0.20 |
| Endrin                    | 100          | 0.25                | 1.58 | 0.67 |
| Heptachlor                | 92           | 0.03                | 33.3 | 6.95 |
| Heptachlor epoxide        | 100          | 0.28                | 1.68 | 0.73 |
| Hexachlorobenzene         | 100          | 0.35                | 1.59 | 0.66 |
| Pentachloronitrobenzene   | 96           | 0.04                | 0.27 | 0.15 |
| Perthane                  | 77           | 0.86                | 23.4 | 8.99 |

<sup>a</sup> Dimethyl 2,3,5,6-tetrachloroterephthalate.

concentration of 11%, 14%, and 100%, respectively. These increases reflect the relative amounts of chlorine in the disinfectants. Ozonation, however, reduced the total alkylbenzene concentration by 52%.

Sand filtration had some effect on the total alkylben-

**Table 4. Concentration of alkylbenzenes in the nondisinfected influent.**

| Alkylbenzenes                                | Frequency, % | Concentration, ng/L |      |      |
|--|--------------|---------------------|------|------|
|  |              | Min                 | Max  | Avg  |
| Cumene                                       | 72           | 0.75                | 959  | 80.4 |
| <i>p</i> -Cymene                             | 85           | 0.31                | 13.1 | 1.70 |
| 1,3-Diethylbenzene                           | 92           | 0.39                | 17.0 | 2.54 |
| 1,4-Diethylbenzene                           | 85           | 0.27                | 11.1 | 1.70 |
| Ethylbenzene                                 | 75           | 0.14                | 1985 | 121  |
| 2-Ethyltoluene                               | 100          | 0.60                | 21.5 | 4.08 |
| 3-Ethyltoluene                               | 89           | 1.29                | 51.0 | 9.96 |
| 4-Ethyltoluene                               | 85           | 0.64                | 112  | 10.3 |
| 1,2,3,4-Tetramethylbenzene                   | 98           | 0.58                | 18.2 | 3.87 |
| 1,2,3,5-Tetramethylbenzene                   | 94           | 0.98                | 15.6 | 3.47 |
| 1,2,4,5-Tetramethylbenzene                   | 96           | 0.86                | 14.5 | 3.49 |
| 1,2,3-Trimethylbenzene                       | 100          | 1.89                | 32.5 | 6.73 |
| 1,2,4-Trimethylbenzene                       | 100          | 6.19                | 91.8 | 19.1 |
| 1,3,5-Trimethylbenzene                       | 100          | 1.90                | 43.1 | 8.24 |
| <i>o</i> -Xylene                             | 98           | 5.77                | 1912 | 120  |
| <i>m</i> - and <i>p</i> -Xylene <sup>a</sup> | 96           | 1.18                | 6514 | 256  |

<sup>a</sup> Coeluting peaks.**Table 5. Concentration of normal alkanes in the nondisinfected influent.**

| Alkanes               | Frequency, % | Concentration, ng/L |      |      |
|-----------------------|--------------|---------------------|------|------|
|                       |              | Min                 | Max  | Avg  |
| <i>n</i> -Decane      | 87           | 0.21                | 18.0 | 2.19 |
| <i>n</i> -Undecane    | 89           | 0.01                | 4.93 | 1.59 |
| <i>n</i> -Dodecane    | 96           | 0.24                | 14.3 | 3.23 |
| <i>n</i> -Pentadecane | 94           | 0.29                | 17.5 | 5.34 |
| <i>n</i> -Hexadecane  | 92           | 1.29                | 15.5 | 5.73 |
| <i>n</i> -Heptadecane | 98           | 5.21                | 31.1 | 11.1 |
| <i>n</i> -Nonadecane  | 96           | 1.11                | 8.03 | 3.21 |
| <i>n</i> -Eicosane    | 70           | 1.80                | 114  | 33.6 |

zene concentration. Removals of 49% and 37% were observed for the nondisinfected and chlorine systems, possibly by biodegradation, although the chlorine concentration remained 20% greater than that of the nondisinfected influent. Alkylbenzene loading on the chlorine GAC columns was considerably greater than that on the other GAC columns. GAC removed, on average, 73% of the alkylbenzenes in the chlorine stream (43% compared to the nondisinfected influent). No additional removal by GAC was noted for the ozone stream, but 40 to 45% concentration reductions by GAC relative to the nondisinfected influent were observed for the chlorine dioxide and chloramine systems.

## Total Alkane

Total alkanes evaluated consisted of a summation of all the normal alkanes listed in Table 5. The total alkane concentration in the nondisinfected influent averaged 50 ng/L with a range of 10 to 150 ng/L. Ozonation reduced the concentration of the total alkanes by an average of 35%. Addition of the other disinfectants had no effect on the total alkane concentration. No reductions in the total alkane concentrations were observed after sand filtration. Similar concentration reductions occurred following GAC treatment for all the streams (44 to 52%).

## Total Phthalate

Total phthalate comprises those phthalates, listed in Table 6, that were monitored during the operational period. The total phthalate concentrations in the nondisinfected influent ranged from 70 to 470 ng/L with an

**Table 6. Concentration of phthalates in the nondisinfected influent.**

| Phthalate                 | Frequency, % | Concentration, ng/L |      |      |
|---------------------------|--------------|---------------------|------|------|
|                           |              | Min                 | Max  | Avg  |
| Diethyl phthalate         | 96           | 28.1                | 98.6 | 53.7 |
| Dipropyl phthalate        | 49           | 0.62                | 11.4 | 3.38 |
| Diisobutyl phthalate      | 98           | 2.45                | 14.5 | 6.89 |
| Dibutyl phthalate         | 98           | 17.5                | 362  | 72.1 |
| 1,2-Butylbenzyl phthalate | 92           | 2.38                | 32.0 | 10.1 |
| Di-2-ethylhexyl phthalate | 77           | 0.59                | 29.7 | 4.54 |
| Diocetyl phthalate        | 94           | 4.18                | 103  | 34.0 |

**Table 7. Concentration of chlorobenzenes and nitrobenzenes in the nondisinfected influent.**

| Benzene derivative      | Frequency,<br>% | Concentration, ng/L |      |      |
|-------------------------|-----------------|---------------------|------|------|
|                         |                 | Min                 | Max  | Avg  |
| Chlorobenzenes          |                 |                     |      |      |
| 1,2-Dichlorobenzene     | 89              | 0.73                | 24.0 | 7.54 |
| 1,3-Dichlorobenzene     | 64              | 0.05                | 8.00 | 1.89 |
| 1,4-Dichlorobenzene     | 94              | 1.41                | 62.1 | 9.85 |
| 1,2,4-Trichlorobenzene  | 72              | 0.61                | 20.2 | 6.20 |
| 1-Chloro-2-nitrobenzene | 91              | 5.91                | 80.5 | 26.2 |
| 1-Chloro-4-nitrobenzene | 91              | 0.48                | 214. | 61.2 |
| Nitrobenzenes           |                 |                     |      |      |
| Nitrobenzene            | 64              | 1.1                 | 53.  | 9.5  |
| 2-Nitrotoluene          | 94              | 0.1                 | 5.6  | 2.6  |
| 2,4-Dinitrotoluene      | 89              | 0.9                 | 260. | 18.  |

average of 180 ng/L. Ozonation produced an average total phthalate reduction of 11%. No significant changes occurred in total phthalate levels associated with the other disinfectants. Average reductions of 20, 4, 10, 20, and 10% occurred after sand filtration in the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine systems, respectively, possibly because of biodegradation. Average removals by GAC were 44 to 50% for each system.

### Total Chlorobenzene and Nitrobenzene

Total chlorobenzene and total nitrobenzene consisted of those compounds listed in Table 7. Total chlorobenzene concentrations in the nondisinfected influent ranged from 4 to 304 ng/L with an average of 100 ng/L. Nitrobenzene concentrations ranged from a minimum of 0.1 ng/L for 2-nitrotoluene to 260 ng/L for 2,4-dinitrotoluene. Ozonation produced an average 68% concentration reduction for total chlorobenzene and 61% for total nitrobenzene. Conversely, chlorination resulted in a 75% increase in total chlorobenzene and a 43% increase in total nitrobenzene. An average total chlorobenzene reduction of 26% occurred following sand filtration in the chlorinated system, possibly by biodegradation, but the effluent concentration remained 43% greater than that of the nondisinfected influent. No reduction in total nitrobenzene was observed. The effluent concentrations from the GAC were comparable for those of all disinfectant systems, with removals ranging from 93 to 96% for the total chlorobenzene and 81 to 92% for total nitrobenzene.

### Other Nonvolatile Organics

Two alkylaldehydes, octanal and nonanal, were quantified. When summed, these two constituents had a nondisinfected influent range from below detection to 37 ng/L, with an average of 14 ng/L. An average uniform increase in the total alkylaldehyde of 144% was observed for ozonation, whereas a relatively nonuniform increase of 56% occurred for the chlorine system relative to the nondisinfected influent. Average reductions of 62% and

26% were observed, respectively, across the sand columns of the ozone and chlorine streams relative to their respective influents. Essentially, no reductions were observed for GAC adsorption.

Other nonvolatile organics monitored included tributyl phosphate, triphenylmethane, 4-nonylphenol, and *d*-fenchone. Table 8 summarizes the effect of disinfection and treatment for these compounds.

## Summary and Conclusions

An on-site pilot plant at Jefferson Parish, LA was constructed to evaluate, during a 1-year period, four different disinfectants (ozone, chlorine dioxide, chloramine, and chlorine) during parallel operation. Various organics, including surrogates such as TOC and TOX, were evaluated to investigate the effects of disinfection and treatment by sand and GAC filtration.

Flame ionization detection and electron capture profiles generally showed that chlorination and chloramination produced more peaks in the low molecular weight range of the chromatogram than the other disinfectants when compared to nondisinfection. Conversely, ozonation produced fewer peaks when compared to nondisinfection for the entire molecular range evaluated. Ozonation reduced the TOC and average instantaneous TOX concentrations by 0.3 mg/L and 10 µg/L, respectively. The average concentration of TOC for the other disinfectants was comparable to that associated with nondisinfection (3.3 mg/L). The average instantaneous TOX concentration for chlorine dioxide, chloramine, and chlorine disinfection after 30 min contact time increased by 60, 92, and 238 µg/L, respectively, from a nondisinfected concentration of 25 µg/L.

The volatile organics most affected by disinfection (chlorination) were the trihalomethanes. After 30 min contact time, average THM concentrations were 1 µg/L, 1 µg/L, 4 µg/L, and 34 µg/L, respectively, for the ozone, chlorine dioxide, chloramine, and chlorine systems. No significant change in concentration was noted after disinfection for other volatile organics evaluated, such as 1,2-dichloroethane, dichloromethane, trichloroethylene, 1,1,2-trichloroethane, and carbon tetrachloride.

Nonvolatile organics evaluated consisted of atrazine, alachlor, other total chlorinated hydrocarbon insecticides, total alkylbenzenes, total alkanes, total phthalates, total chlorobenzenes, total nitrobenzenes, total alkylaldehydes, and others. Ozonation produced an average concentration reduction of 83, 84, 57, 52, 35, 11, 68, and 61%, respectively, for atrazine, alachlor, total CHI, total alkylbenzenes, total alkanes, total phthalates, total chlorobenzenes, and total nitrobenzenes. Conversely, an average increase of 144% was observed for the total alkylaldehydes, octanal and nonanal, after ozonation. Sand filtration reduced this concentration essentially to the concentration level of the nondisinfected sand-filtered effluent.

Chlorination produced no concentration change for



Table 8. Data for some selected nonvolatile organics.

| Compound           | Concentration, ng/L |      | Disinfection |                    | Sand                |                    | GAC                 |  |
|--------------------|---------------------|------|--------------|--------------------|---------------------|--------------------|---------------------|--|
|                    | Min                 | Max  | Avg          | O <sub>3</sub> , % | Cl <sub>2</sub> , % | O <sub>3</sub> , % | Cl <sub>2</sub> , % | O <sub>3</sub> , % Cl <sub>2</sub> , % |
| Tributylphosphate  | 9.4                 | 158. | 40.7         | 89R <sup>a</sup>   | NE <sup>b</sup>     | NE                 | NE                  | (96-98)R                               |
| Triphenylmethane   | 0.83                | 21.4 | 3.3          | 38R                | 26R                 | 53R                | NE                  | (52-65)R                               |
| 4-Nonylphenol      | 5.2                 | 207. | 59.5         | 72R                | 54R                 | NE                 | NE                  | NE (74-82R)                            |
| <i>d</i> -Fenchone | 0.36                | 17.7 | 5.6          | 59R                | 133I <sup>c</sup>   | NE                 | 40R                 | (80-94)R                               |

<sup>a</sup> R = removal.<sup>b</sup> NE = no effect.<sup>c</sup> I = increase.

atrazine, alachlor, total CHI, total alkanes, and total phthalates. An increase in concentration was observed after chlorination for total alkylbenzenes, total chlorobenzenes, total nitrobenzenes, and total alkylaldehydes of 100, 75, 43, and 56%, respectively. No significant concentration change was observed for atrazine, alachlor, total CHI, total alkanes, total phthalates, total chlorobenzenes, total nitrobenzenes, and total alkylaldehydes after disinfection with chloramine and chlorine dioxide. A slight concentration change was noted for the other nonvolatiles.

Sand filtration had some effect on the total alkylbenzenes, total phthalates, total chlorobenzenes, and total alkylaldehydes, with lower concentrations in the effluent as compared to the influent. GAC removed the volatile organics for a period of time (usually < 100 days) before breakthrough. GAC effectively removed the chlorinated hydrocarbons, total alkylbenzenes, total alkanes, total chlorobenzenes, total nitrobenzenes, and total alkylaldehydes for the 1-year operational period. The total phthalates were effectively removed for about 250 days before the ozonated stream broke through.

Of the disinfection streams evaluated, ozone appears to be the disinfectant of choice because lower concentrations of organics were detected during its use. However, what happens to the organics after ozonation remains uncertain. Are these organics oxidized and destroyed, are they converted to other organics that are more biodegradable, and are they more water soluble and not extractable, making them nondetectable?

Consequently, more research is needed before the performance and cost aspects of disinfection can be understood more fully.

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## REFERENCES

1. U.S. EPA. National interim primary drinking water regulations; control of trihalomethanes in drinking water, final rule. 40 CFR Part 141, 1979.
2. Miller, R. G., Kopfler, F. C., Condie, L. W., Pereira, M. A., Meier, J. R., Ringhand, H. P., Robinson, M., and Casto, B. C. Results of toxicological testing of Jefferson Parish Pilot Plant samples. Paper presented at Second International Symposium on Health Effects of Drinking Water Disinfectants and Disinfection By-Products, August 27-29, 1985.
3. U.S. EPA. A Multiple Process Approach for Removal of Organic Substances from Drinking Water. Cooperative Agreement CS806925, October 1979.
4. U.S. EPA. Quality Assurance Plan, A Multiple Process Approach for Removal of Organic Substances from Drinking Water. Cooperative Agreement CS806925, November 1982.